RECEIVED BY DTIC AUG 21 1970

MASTER

C00-1488-19

THEORY OF HYPERFINE ESR LINEWIDTH

IN A LINEAR CHAIN: $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$

Carl D. McElwee

June 30, 1970

Technical Report C00-1488-19

Under

United States Atomic Energy Commission Contract AT(11-1)1488

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

24

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THEORY OF HYPERFINE ESR LINEWIDTH
IN A LINEAR CHAIN: $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$

C. D. McElwee

I. INTRODUCTION

The Heisenberg Hamiltonian has been used extensively as a model for explaining the magnetic properties of solids.

$$\mathcal{H}_{\text{ex}} = -J_{ij} \vec{S}_i \cdot \vec{S}_j \quad J_{ii} = 0$$

The coupling between spins is either ferromagnetic or antiferromagnetic depending on whether J is positive or negative, respectively. This Hamiltonian cannot be solved in closed form even in one dimension. Bonner and Fisher¹ have numerically calculated the eigenvalues of finite linear chains and computed the various thermodynamic functions. Their results are extrapolated to obtain the infinite chain limit. Griffiths² has used their results to show that the specific heat and magnetic susceptibility data for $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ (CTS) can be explained by assuming there are exchange coupled linear chains of copper ions parallel to the crystalline C axis. It was assumed that an isotropic Heisenberg Hamiltonian of the form

$$\mathcal{H}_{\text{ex}} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} \quad (1)$$

described the linear chain coupling and J was found to be -3.15°K .

Carboni and Richards³ have calculated the dipolar contribution to the ESR linewidth in this linear chain material to be about 10 Oe for the full width at half maximum. This is much less than the experimental data of Abe and Ono⁴ who

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

report a total experimental linewidth of 30 Oe for H_0 (external static magnetic field) along the C axis at 13.2 GHz. It would appear then, that there is another interaction which is contributing significantly to the linewidth.

In the process of their linewidth calculation, Carboni and Richards made exact numerical calculations of the frequency dependent two spin correlation functions in finite Heisenberg linear chains. Their results, in histogram form, suggest a divergence near zero frequency. If there really is a divergence then the lineshape formalism used by Carboni and Richards, which assumes exchange narrowing and, implicitly, that the zero frequency correlation functions are finite, cannot accurately describe the lineshape in the linear chain. This unusual behavior near zero frequency could have a pronounced effect upon the hyperfine contribution to the ESR linewidth which involves only two spin correlation functions. Physically, the divergence near zero frequency means that the exchange interaction is not modulating the electron spins as effectively as expected. Therefore, the exchange narrowing may not be so pronounced and the linewidth broader than expected. This is the motivation for studying the hyperfine ESR linewidth in this linear chain material.

II. LINESHAPE FORMALISM

In describing the linear response of a magnetic system to a small r.f. magnetic field of frequency ω , applied along the x direction, the following equations are obtained⁵.

$$\chi(\omega) = \frac{\langle M_x \rangle}{H(\omega)} = \int_0^\infty G(\tau) e^{-i\omega\tau} d\tau \quad (2)$$

$$G(\tau) = \frac{i}{\hbar} \langle [M_x(\tau), M_x] \rangle \quad (3)$$

$\chi(\omega)$ is the magnetic susceptibility, H is the r.f. field, and $G(\tau)$ is the Green's function. Quantum statistical averages are implied by $\langle \rangle$. The time dependent operator $M_x(\tau)$ is in the usual Heisenberg representation.

$$M_x(\tau) = e^{i\mathcal{H}\tau/\hbar} M_x e^{-i\mathcal{H}\tau/\hbar} \quad (4)$$

If $\chi(\omega)$ is broken down into its real and imaginary parts

$$\chi = \chi' - i\chi'' \quad (5)$$

it is possible to show that⁶

$$\chi''(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{1}{2\hbar} \int_{-\infty}^{\infty} \langle [M_x(t), M_x]_+ \rangle e^{-i\omega t} dt \quad (6)$$

where $\beta = (kT)^{-1}$. In the high temperature approximation, $\beta\hbar\omega \ll 1$, equation (6) becomes

$$\frac{\chi''(\omega)}{\omega} \approx \frac{\beta}{4} \int_{-\infty}^{\infty} \langle [M_x(t), M_x]_+ \rangle e^{-i\omega t} dt. \quad (7)$$

$\chi''(\omega)/\omega$ is the usual lineshape function found in the literature.

The task now is to calculate the quantities on the right side of equation (7) from a detailed consideration of the system. In practice, seldom can this be done exactly for interesting physical systems. Perturbation theory must be applied to obtain approximate results. Usually, the Hamiltonian of the system can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad (8)$$

$\mathcal{H}'$ is considered a small interaction and treated as a perturbation. In this case, $\mathcal{H}_0$ contains the Zeeman and the exchange interactions while $\mathcal{H}'$ is the hyperfine interaction. It is assumed that $\mathcal{H}'$ disturbs the system from equilibrium only slightly so that the density operator is

$$\rho \approx \rho_0 = e^{-\beta \mathcal{H}_0} / \text{Tr } e^{-\beta \mathcal{H}_0} \quad (9)$$

A new operator is defined by the following equation.

$$M_+(t) = e^{i\mathcal{H}_0 t/\hbar} \tilde{M}_+(t) e^{-i\mathcal{H}_0 t/\hbar} \quad (10)$$

From the equation of motion for $\tilde{M}_+(t)$, it is possible to obtain the following^{5,6}

$$\frac{d}{dt} \langle \tilde{M}'_+(t) M_- \rangle = \frac{i}{\hbar} \langle [\mathcal{H}', M_+] M_- \rangle - \frac{1}{\hbar^2} \int_0^t \langle [\mathcal{H}', [\mathcal{H}'(\tau), M_+]] M_- \rangle d\tau \quad (11)$$

$$\mathcal{H}'(t) = e^{i\mathcal{H}_0 t/\hbar} \mathcal{H}' e^{-i\mathcal{H}_0 t/\hbar} \quad (12)$$

$\langle \tilde{M}_+(t) M_- \rangle$ as calculated from equation (11) is related to $\langle M_+(t) M_- \rangle$ by

$$\langle M_+(t) M_- \rangle = \langle \tilde{M}_+ e^{-i\mathcal{H}_0 t/\hbar} M_- e^{i\mathcal{H}_0 t/\hbar} \rangle = e^{i\omega_0 t} \langle \tilde{M}_+(t) M_- \rangle \quad (13)$$

where ω_0 is the Zeeman frequency. The above result is a consequence of the exchange part of $\mathcal{H}_0$ commuting with M_- .

For the system under consideration

$$\mathcal{H}_0 = -\gamma_n H_0 \sum_j I_j^z + \gamma_e H_0 \sum_j S_j^z - 2J \sum_j \vec{S}_j \cdot \vec{S}_{j+1} \quad (14)$$

$$\mathcal{H}' = \sum_j \vec{I}_j \cdot \vec{\mathcal{R}} \cdot \vec{S}_j = \sum_j \mathcal{R}_{\alpha\beta} I_j^\alpha S_j^\beta \quad \alpha, \beta = +, -, z \quad (15)$$

where H_0 is the external static magnetic field, γ_n and γ_e are respectively the nuclear and electronic gyromagnetic ratios, J is the exchange constant, and $\vec{\mathcal{R}}$ is the hyperfine interaction tensor. Using this $\mathcal{H}_0$ and $\mathcal{H}'$ the various commutators and expectation values in equation (11) must be evaluated. $\langle [\mathcal{H}', S^+] S^- \rangle$ is zero in the high temperature approximation. If the Zeeman interaction is neglected in the density operator for electrons compared to the exchange interaction, then $\langle S^+(\tau) S^- \rangle = 2 \langle S^z(\tau) S^z \rangle$ since the system is isotropic and equation (11) becomes

$$\frac{d}{dt} \langle \tilde{M}_+(t) M_- \rangle = -\gamma_e^2 \frac{2}{3} I(I+1) \int_0^t [\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}] \times \sum_j \langle S_j^z(\tau) S_j^z \rangle d\tau. \quad (16)$$

$\mathcal{R}^2 = 2\mathcal{R}_{+z}^2 + \mathcal{R}_{zz}^2 + 2\mathcal{R}_{-z}^2$, $\mathcal{R}'^2 = 4\mathcal{R}_{+-}^2 + 2\mathcal{R}_{z-}^2 + 4\mathcal{R}_{--}^2$, $\omega_0 = \gamma_e H_0$, and I is the nuclear spin. If all $\langle S_i^z(\tau) S_i^z \rangle$ are independent of i and the high temperature limit of $(2/3)\gamma_e^2 S(S+1)$ is used for $\langle M_+ M_- \rangle$ then

$$\frac{d}{dt} \left[\frac{\langle \tilde{M}_+(t) M_- \rangle}{\langle M_+ M_- \rangle} \right] = - \frac{I(I+1)}{S(S+1)} \int_0^t [\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}] \langle S^z(\tau) S^z \rangle d\tau. \quad (17)$$

It has been assumed that $\gamma_n H_0 \tau = \omega_n \tau \ll 1$ for τ such that $\langle S^z(\tau) S^z \rangle$ is non zero.

Integrating equation (17) gives the following form.

$$\frac{\langle \tilde{M}_+(t) M_- \rangle}{\langle M_+ M_- \rangle} = 1 - \frac{I(I+1)}{S(S+1)} \int_0^t \int_0^{t'} \langle S^z(\tau) S^z \rangle [\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}] d\tau dt' \quad (18)$$

Following Kubo and Tomita⁷ it is assumed that equation (18) describes short time behavior and a solution of the form $e^{-\psi(\tau)}$ which is consistent for short times is found.

$$\frac{\langle \tilde{M}_+(t) M_- \rangle}{\langle M_+ M_- \rangle} = \exp \left[- \frac{I(I+1)}{S(S+1)} \int_0^t \int_0^{t'} \langle S^z(\tau) S^z \rangle (\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}) d\tau dt' \right] \quad (19)$$

III. FREQUENCY DEPENDENT SELF-CORRELATION FUNCTION

In order to carry the analysis further it is necessary to know $\langle S^z(\tau) S^z \rangle$, the two spin time correlation function. Carboni and Richards³ have calculated $\langle S^z(\tau) S^z \rangle_\omega$, the frequency transform of $\langle S^z(\tau) S^z \rangle$, numerically from quantum mechanical first principles. Their results strongly suggest a divergence near ω equal to zero. It is not possible to state definitely since only histograms

are calculated. If one assumes spin diffusion is occurring in the system, it is possible to show that the Fourier space-time transform of $\langle S^z(\tau) S^z \rangle$ is given by

$$\langle S_i^z(\tau) S_j^z \rangle_{k,\omega} = \frac{S(S+1)}{3\pi} \frac{Dk^2}{D^2k^4 + \omega^2} \quad (20)$$

D is the spin diffusion constant, k is the wave vector, and S is the electron spin. This assumption gives a divergence of $\langle S_i^z(\tau) S_i^z \rangle_{\omega}$ for small ω as $|\omega|^{-1/2}$ but does not reproduce Carboni and Richards' results over the whole frequency range. No divergence is predicted for three dimensional systems.

Fernandez and Gersch⁸ have assumed that $\langle S_i^z(\tau) S_j^z \rangle_{k,\omega}$ is a sum of a Gaussian and a cut-off Lorentzian with weighting factors to make the Gaussian dominant at large k and the Lorentzian, the diffusion result, dominant at small k . Using this construction they are able to obtain fair agreement with Carboni and Richards. In addition, they are able to show that the divergence is at least as severe as $\ln|\omega|^{-1}$, provided $\langle S_i^z(\tau) S_j^z \rangle_{k,\omega}$ is a monotonically decreasing function of $|\omega|$ at small k .

It would appear that the divergence in $\langle S^z(\tau) S^z \rangle_{\omega}$ is actually present near $\omega = 0$ for one dimensional systems and is due to a spin diffusion process for small k and ω but modifications are necessary in order to reproduce Carboni and Richards' results over the whole frequency interval. Recently, Tahir-Kheli and McFadden⁹ have had good success in this endeavor through the method of generalized diffusivity¹⁰. This method reduces to the spin diffusion result for small k and ω . The generalized diffusivity is represented by a two parameter Gaussian, the parameters being determined by the known second and fourth frequency

moments of $\langle S_i^z(\tau) S_j^z \rangle_{k, \omega}$. In the following discussion this method has been employed to calculate $\langle S_i^z(\tau) S_i^z \rangle_{\omega}$.

In light of the previous discussion it is assumed that $\langle S^z(\tau) S^z \rangle_{\omega}$ goes as $|\omega|^{-1/2}$ for small ω . $\langle S^z(\tau) S^z \rangle_{\omega}$ as calculated by the method of generalized diffusivity can be fitted well to the form

$$f(\omega) = \frac{\hbar^2 A}{|\omega|^{1/2}} + B\hbar^2 \quad (21)$$

out to about $\omega = 2.5J$. A least squares fit gives $A = .02J^{-1/2}$ and $B = .0122J^{-1}$. For larger ω , $\langle S^z(\tau) S^z \rangle_{\omega}$ starts to fall off rapidly. This region shall be approximated by a straight line.

$$\langle S^z(t) S^z \rangle_{\omega} \cong \begin{cases} \hbar^2 A |\omega|^{-1/2} + B\hbar^2 & |\omega| \leq \omega_e \\ \frac{f(\omega_e) \omega_e}{\omega_e - \omega_e} \left(1 - \frac{|\omega|}{\omega_e}\right) & \omega_e \leq |\omega| \leq \omega_c \\ 0 & |\omega| \geq \omega_c \end{cases} \quad (22)$$

The actual curve as calculated by the method of generalized diffusivity is shown as a full curve in fig. 1. The approximation of equation (22) is shown as a dashed curve with $\omega_e = 2.88J$ and $\omega_c = 4.5J$.

IV. LINESHAPE CALCULATIONS

In order to obtain the lineshape it is necessary to take the Fourier transform of equation (22) and integrate twice with respect to time as dictated by

Fig. 1: $\langle S^z(t) S^z \rangle_\omega$ as calculated by generalized diffusivity is shown as a solid curve. The approximation of equation (22) is drawn as a dashed curve.

equation (19). Doing this, the following forms result for long times.

$$\int_0^t \int_0^{\tau} \langle S^z(t') S^z \rangle dt' d\tau \xrightarrow{\omega_c t \gg 1} \frac{4}{3} \sqrt{2\pi} A \hbar^2 |t|^{3/2} + \pi B \hbar^2 |t|$$

$$\int_0^t \int_0^{\tau} e^{-i\omega_0 t'} \langle S^z(t') S^z \rangle dt' d\tau \xrightarrow{\omega_c t \gg 1} \pi B \hbar^2 |t| + \frac{\pi A \hbar^2}{\omega_0^{1/2}} (1-i) |t| \quad (23)$$

If ω_0 is too small, equation (23) will have to be revised but it is applicable at 13.2GHz, the frequency of major interest here. The imaginary part is responsible only for a shift in the resonance frequency, so we neglect it. From equations (13) and (19) the following result for $\langle M_+(t) M_- \rangle$ is obtained.

$$\langle M_+(t) M_- \rangle \xrightarrow{\omega_c t \gg 1} \langle M_+ M_- \rangle \exp \left[i\omega_0 t - \gamma_1 |t| - (\gamma_2 |t|)^{3/2} \right] \quad (24)$$

$$\gamma_1 = \pi B \hbar^2 \frac{I(I+1)}{S(S+1)} (\mathcal{R}^2 + \mathcal{R}'^2) + \frac{\pi A \hbar^2}{\omega_0^{1/2}} \frac{I(I+1)}{S(S+1)} \mathcal{R}'^2$$

$$\gamma_2 = \left[\frac{4}{3} \sqrt{2\pi} A \hbar^2 \mathcal{R}^2 \frac{I(I+1)}{S(S+1)} \right]^{3/2} \quad (25)$$

Equation (24) holds if $\omega_c t \gg 20$ but $\exp \left[-\gamma_1 \frac{20}{\omega_c} - (\gamma_2 \frac{20}{\omega_c})^{3/2} \right] \approx 1$ so this is the justification for using it for all times. The expectation value of the anticommutator appearing in equation (7) is given by

$$\langle [M_x(t), M_x]_+ \rangle = \frac{1}{2} \langle M_+ M_- \rangle \left[e^{i\omega_0 t} + e^{-i\omega_0 t} \right] e^{-\gamma_1 |t| - (\gamma_2 |t|)^{3/2}} \quad (26)$$

The quantities γ_1 and γ_2 determine the linewidth and lineshape. If $\mathcal{R}$ and $\mathcal{R}'$ are known, numerical values for γ_1 and γ_2 can be obtained and the lineshape function can be calculated numerically from equations (7) and (26).

Rogers¹¹ has measured the hyperfine constants for Cu^{++} in the tetramine complex to be $\mathcal{R}_{||} = 209 \text{ Oe}$ and $\mathcal{R}_{\perp} = 32 \text{ Oe}$. The symbol $||$ refers to the Z axis of the complex, which is taken to be the line joining the H_2O molecules. The Z axis of the complex lies in the b-c plane of the crystal unit cell and makes an angle of $26^\circ 20' \pm 4^\circ$ ¹² with the C axis of the crystal, as shown graphically in fig. 2. With this information $\mathcal{R}$ and $\mathcal{R}'$ can be calculated for various directions of H_0 the external magnetic field. In particular, two cases will be considered: $\text{H}_0 || a$ and $\text{H}_0 || c$.

Performing the transformation into the laboratory system for $\text{H}_0 || a$, the following results are obtained for $\mathcal{R}$ and $\mathcal{R}'$.

$$\begin{aligned}\mathcal{R} &= \mathcal{R}_{\perp} = 32 \text{ Oe} \\ \mathcal{R}' &= \left[(\mathcal{R}_{||}^2 + \mathcal{R}_{\perp}^2) / 2 \right]^{1/2} = 149.5 \text{ Oe}\end{aligned}\quad (27)$$

At a resonance frequency of 13.2 GHz equation (25) gives $\gamma_1 = .0267\mathcal{R}$ and $\gamma_2 = .0534\mathcal{R}$. The resulting lineshape is plotted in fig. 3. Gaussian and Lorentzian lines of the same intensity and half-width are plotted for reference. The full width of the line at half maximum is about $.192\mathcal{R} = 6.14 \text{ Oe}$. The ESR linewidth reported by Rogers¹³ at 13.2 GHz is 17.2 Oe. Carboni and Richards³ have calculated the dipolar contribution to be 9.6 Oe. Reasonably then, one would expect the hyperfine interaction to be about 7.6 Oe. This compares favorably with our calculation of 6.14 Oe.

Similarly for $\text{H}_0 || c$ we obtain

$$\begin{aligned}\mathcal{R} &= 188 \text{ Oe} \\ \mathcal{R}' &= 71.5 \text{ Oe}\end{aligned}\quad (28)$$

$$\mathcal{H} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}$$

Fig. 2: The crystal structure of CTS.

Fig. 3: Resonance lineshape for $H_0||a$ at 13.2 GHz.

Again at 13.2 GHz equation (25) gives $\gamma_1 = .00256\mathcal{R}$ and $\gamma_2 = .0963\mathcal{R}$. As shown in fig. 4, the resultant lineshape has a full width at half maximum of $.280\mathcal{R} = 52.6$ Oe. No experiment has observed a linewidth along the C axis anywhere near 52.6 Oe. Abe and Ono⁴ report a total experimental linewidth for $H_0 \parallel C$ at 9.6 GHz of about 31 Oe. This unusually large hyperfine contribution is a direct consequence of the divergence of the frequency dependent two spin correlation function near zero frequency.

V. INTERCHAIN COUPLING

A strict linear chain material is not expected to have a Néel point but CTS does at about $.37^\circ$ K as indicated by a sharp spike on the specific heat curve. This indicates the presence of weak exchange coupling (J') between chains. None of the theoretical arguments which predict a divergence in one dimensional systems do so in three dimensional systems. The weak interchain exchange coupling is then expected to limit the divergence at zero frequency and possibly lower the hyperfine contribution to the linewidth. Oguchi¹⁴ has estimated this coupling to be about one hundredth the strong intrachain coupling on the basis of Green's function theory for the Néel temperature. Using the method of generalized diffusivity to calculate the frequency dependent self-correlation function for such an interchain exchange coupling, it is found that the divergence is indeed destroyed but that the rise near zero frequency is still too large to appreciably lower the hyperfine contribution. The transverse diffusion constant D_2 is proportional to J'^2/J and the $|\omega|^{-1/2}$ divergence is destroyed for $\omega \in J'/J \approx 10^{-4}J$. Thus, the interchain coupling alters the $|\omega|^{-1/2}$

LINESHAPE AMPLITUDE

Fig. 4: Resonance lineshape for $H_0 \parallel c$ at 13.2 GHz.

divergence only for very small frequencies and the zero frequency component of the self-correlation function is still quite large. In another equivalent point of view, the $|t|^{3/2}$ time dependence of equation (24) is destroyed for $t \gtrsim \frac{J}{J^2} \approx \frac{10^4}{J}$. For greater times the exponential decays as $|t|$. However, at $t = \frac{10^4}{J}$ the exponential has decayed to such a small value that its decay for larger times is unimportant in determining the linewidth.

If as indicated above an interchain coupling of $.01J$ is not sufficient to reduce the hyperfine linewidth, the question arises as to what magnitude of J' one must use to bring the linewidth into the range of experimental results? If one uses $J' = .1J$ in the method of generalized diffusivity to calculate the frequency dependent self-correlation function, it is found that departure from the $|\omega|^{-1/2}$ dependence occurs at $\omega \lesssim 2 \times 10^{-2} J \propto \frac{J^2}{J'}$. Similarly, for $t \gtrsim \frac{10^2}{2J}$ the $|t|^{3/2}$ time dependent of equation (24) is destroyed. The lineshape is given by the Fourier transform of the following function.

$$\begin{cases} \exp\left[-r_1|t| - (r_2|t|)^{3/2}\right] & t \lesssim \frac{10^2}{2J} \\ \exp\left[-r_1|t| - \frac{3}{2}r_2^{3/2}\frac{10}{\sqrt{2J}}|t| + \frac{r_2^{3/2}}{2}\left(\frac{10^2}{2J}\right)^{3/2}\right] & t \gtrsim \frac{10^2}{2J} \end{cases} \quad (29)$$

For both $H_0 \parallel a$ and $H_0 \parallel c$

$$\exp\left[-r_1\frac{10^2}{2J} - \left(r_2\frac{10^2}{2J}\right)^{3/2}\right] \approx 1 \quad (30)$$

This indicates that the lineshape is determined primarily by the Fourier transform of

$$\exp\left[-\gamma_1|t| - \frac{3}{2} \gamma_2^{3/2} \left(\frac{10^2}{2J}\right)^{1/2} |t|\right], \quad (31)$$

which results in a Lorentzian line with full width

$$\Delta = 2 \left[\gamma_1 + \frac{3}{2} \gamma_2^{3/2} \left(\frac{10^2}{2J}\right)^{1/2} \right] \quad (32)$$

For $H_0 || a$ at 13.2 GHz the linewidth is $\Delta = .064\mathcal{R} = 2.0$ Oe. Again at 13.2 GHz but for $H_0 || c$ the linewidth is $\Delta = .062\mathcal{R} = 12$ Oe. If one adds to these values the 10 Oe dipolar contribution calculated by Carboni and Richrds, the total theoretical linewidths are 12 Oe for $H_0 || a$ and 22 Oe for $H_0 || c$ at 13.2 GHz. This is to be compared with the linewidths of 31 Oe for $H_0 || c$ and 20 Oe for $H_0 || a$ reported by Abe and Ono at 9.6 GHz and 17.2 Oe reported by Rogers for $H_0 || a$ at 13.2 GHz.

Thus, for $J' = .1J$ the theoretical predictions are below the experimental values. Unfortunately, the Néel point of 1.6° K as predicted by Oguchi's theory for $J' = .1J$ is much too large. There is then an inconsistency in the prediction of the interchain coupling based on ESR linewidths and alternately the Néel point.

One might suppose that the dipolar or hyperfine interaction could enter the calculation to limit the divergence while having little effect on the Néel point.

This appears not to be the case since both enter the calculation in the same manner as J' and they are smaller than the necessary J' . Our earlier results indicated that a J' of .01J was not sufficient to limit the divergence. J is 2.35×10^4 Oe in magnetic field units, so an interaction of 235 Oe will not suffice. The hyperfine interaction is 209 Oe. The nearest off chain neighbor in CTS is $7 \text{ \AA}$ away giving a dipole interaction of about 30 Oe. Thus, both interactions are too small to limit effectively the divergence near zero frequency.

VI. SELF-CONSISTENT CALCULATION

Since experiment indicates that the hyperfine contribution cannot be anywhere near 53 Oe, something must be limiting the divergence of $\langle S_1^z(\tau) S_1^z \rangle_\omega$ near zero frequency. In other words $\langle S_1^z(\tau) S_1^z \rangle$ will decay faster than indicated by the linear chain results. If $\langle S_1^z(\tau) S_1^z \rangle$ decays rapidly enough then $\langle \tilde{M}_+(\tau) M_- \rangle / \langle M_+ M_- \rangle$ of equation (19) will have an exponential time dependence. We assume this is the case and put a factor of $e^{-\eta t}$ on both sides of equation (19).

$$\frac{\langle \tilde{M}_+(t) M_- \rangle}{\langle M_+ M_- \rangle} = e^{-\eta t} = \exp \left[-\frac{I(I+1)}{S(S+1)} \int_0^t \int_0^{t'} \langle S_1^z(\tau) S_1^z \rangle (\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}) e^{-\eta \tau} d\tau dt' \right] \quad (33)$$

Equation (33) is now solved self-consistently for η . If $\langle S^z(\tau) S^z \rangle e^{-\eta \tau}$ decays rapidly enough the upper limit of t' can be extended to infinity.

$$\eta t = \frac{I(I+1)}{S(S+1)} \int_0^t \int_0^\infty \langle S_1^z(\tau) S_1^z \rangle (\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}) e^{-\eta \tau} d\tau dt' \quad (34)$$

$$\eta = \frac{I(I+1)}{S(S+1)} \int_0^\infty \langle S_1^z(\tau) S_1^z \rangle (\mathcal{R}^2 + \mathcal{R}'^2 e^{-i\omega_0 \tau}) e^{-\eta \tau} d\tau$$

Assuming $\omega_0 \gg \eta$ and neglecting an imaginary part which represents a shift in resonance frequency we have

$$\eta = \frac{I(I+1)}{S(S+1)} \left\{ \frac{\sqrt{2} \pi A \hbar^2}{\eta^{1/2}} R^2 + \frac{\pi A \hbar^2}{\omega_0^{1/2}} R'^2 + B \pi \hbar^3 [R^2 + R'^2] \right\} \quad (35)$$

All the quantities in equation (35) except η have been defined previously and given numerical values.

Solution of equation (35) for $H_0 || c$ gives an η of 22 Oe or a full width at half maximum of 44 Oe. Similarly for $H_0 || a$ η is 2.7 Oe giving a resonance linewidth of 5.4 Oe. These widths are slightly lower than the predictions of 53 Oe and 6 Oe of the strict linear chain but still entirely too large to reconcile with experiment.

VII. TEMPERATURE DEPENDENCE OF THE SELF-CORRELATION FUNCTION

Saito¹⁵ has reported the temperature dependence of the linewidth from room temperature down to liquid He temperatures. His experiments show the linewidth to increase by at least a factor of 5 from room temperature to about 1° K.

Carboni and Richards³ have investigated the temperature dependence of the dipolar linewidth and find it decreases with temperature contrary to Saito's results.

They find that the divergence of the two spin correlation function near zero frequency decreases as the temperature is lowered. If this is correct, then one would expect the hyperfine linewidth to decrease as the temperature is lowered also.

Since Carboni and Richards only calculate histograms, it is difficult to tell what is really happening near zero frequency. We have looked at the temperature dependence of $\langle S_1^z(\tau) S_1^z \rangle_\omega$ through the method of generalized diffusivity.

The generalized diffusivity is represented by a two parameter Gaussian, the parameters being determined by the second and fourth frequency moments defined below.

$$G_k^{(n)} = \sum_{i,j} e^{-i\vec{k} \cdot \vec{r}_{ij}} \left[\left(i \frac{d}{d\tau} \right)^{n-1} \frac{1}{\hbar} \langle [S_i^z(\tau), S_j^z] \rangle \right]_{\tau=0} / G_k^{(0)}$$

$$G_k^{(0)} = \sum_{i,j} e^{-i\vec{k} \cdot \vec{r}_{ij}} \int_{-\infty}^{\infty} \frac{[e^{\beta \hbar \omega} - 1]}{\hbar \omega} \langle S_j^z(t) S_i^z \rangle_\omega d\omega \quad (36)$$

Collins and Marshall¹⁶ have evaluated the second and fourth moments in the high temperature approximation. In order to utilize the method of generalized diffusivity at a finite temperature the second and fourth moments must be known at that temperature. Performing the commutators implied by equation (36) the second and fourth moments can be expressed in terms of static correlations.

$$G_k^{(2)} \cdot G_k^{(0)} = N \sum_{\vec{R}} J_{\vec{R}} \langle S_j^+ S_{j+\vec{R}}^- \rangle (2 - 2 \cos \vec{k} \cdot \vec{R}) \quad (37)$$

$$G_k^{(4)} \cdot G_k^{(0)} = 2N \sum_{\vec{A}, \vec{B}, \vec{R}} J_{\vec{A}} (1 - e^{i\vec{k} \cdot \vec{A}}) \left\{ (J_{\vec{B}} J_{\vec{R}} - J_{\vec{B}} J_{\vec{R}-\vec{B}}) \times \right.$$

$$\begin{aligned}
& (1 - e^{-i\vec{k} \cdot \vec{B}}) + J_{\vec{B}-\vec{R}} J_{\vec{R}} (1 - 2e^{-i\vec{k} \cdot \vec{R}} + e^{-i\vec{k} \cdot \vec{B}}) \Big\} \times \\
& \left\{ 2 \langle S_j^+ S_{j+\vec{R}}^z S_{j+\vec{B}}^z S_{j+\vec{A}+\vec{B}}^- \rangle e^{i\vec{k} \cdot \vec{B}} \right. \\
& \quad + 2 \langle S_j^+ S_{j-\vec{A}}^z S_{j-\vec{A}+\vec{R}}^z S_{j-\vec{A}+\vec{B}}^- \rangle \\
& \quad - \langle S_j^+ S_{j-\vec{A}-\vec{R}}^+ S_{j-\vec{A}}^- S_{j-\vec{A}+\vec{B}-\vec{R}}^- \rangle e^{i\vec{k} \cdot \vec{R}} \\
& \quad \left. - \langle S_j^+ S_{j+\vec{R}}^+ S_{j+\vec{B}}^- S_{j+\vec{A}+\vec{R}}^- \rangle e^{i\vec{k} \cdot \vec{R}} \right\}
\end{aligned} \tag{38}$$

$J_{\vec{R}}$ is the exchange interaction between two electrons on lattice sites separated by the vector $\vec{R}$. The results of Carboni and Richards³ for the static spin correlations, which are expected to be pretty good, are used to evaluate the second and fourth moments at various temperatures for the linear chain, as shown in figures 5 and 6.

The frequency dependent self-correlation functions which result by the use of these moments in the method of generalized diffusivity are shown in fig. 7.

Fig. 5: The second moment $G_K''(2)$ at various temperatures for the linear chain.

Fig. 6: The fourth moment $G_k^{(4)}$ at various temperatures for the linear chain.

Fig. 7: Temperature dependence of the self-correlation function in a linear chain.

It is seen that the divergence near zero frequency decreases as the temperature is lowered as Carboni and Richards' results indicate. However, the decrease with temperature is not nearly as drastic as that of Carboni and Richards. This means that the substantial increase in the linewidth as the temperature is lowered cannot be explained by the behavior of the divergence near zero frequency.

VIII. T_1/T_2 RATIOS

Lastly, we have calculated the ratio of the relaxation time for the Z component of magnetization (T_1) to that for the transverse components (T_2). An equation similar to (11) exists for the Z component of magnetization.

$$\frac{d}{dt} \langle \tilde{M}_z(t) M_z \rangle = \frac{i}{\hbar} \langle [\mathcal{H}', M_z] M_z \rangle - \frac{1}{\hbar^2} \int_0^t \langle [\mathcal{H}', [\mathcal{H}'(\tau), M_z]] M_z \rangle d\tau \quad (39)$$

By a development parallel to that giving equation (17) we obtain

$$\begin{aligned} \frac{d}{dt} \left[\frac{\langle M_z(t) M_z \rangle}{\langle M_z M_z \rangle} \right] &= - \frac{\mathcal{H}'^2 I(I+1)}{S(S+1)} \int_0^t (e^{i\omega_0 \tau} + e^{-i\omega_0 \tau}) \langle S_i^z(\tau) S_i^z \rangle d\tau \\ &= - \frac{\mathcal{H}'^2 I(I+1)}{S(S+1)} \int_{-t}^t e^{i\omega_0 \tau} \langle S_i^z(\tau) S_i^z \rangle d\tau. \end{aligned} \quad (40)$$

Assuming that this describes short time behavior, we have

$$\frac{\langle M_z(t) M_z \rangle}{\langle M_z M_z \rangle} = \exp \left[- \frac{R'^2 I(I+1)}{S(S+1)} \int_0^t \int_{-t'}^{t'} e^{i\omega_0 \tau} \langle S_i^z(\tau) S_i^z \rangle d\tau dt' \right] \quad (41)$$

If $\langle S_i^z(\tau) S_i^z \rangle$ decays as slowly as the strict linear chain results indicate, then we should not extend the limits of the t' integral to infinity. However, the experimental linewidths indicate that $\langle S_i^z(\tau) S_i^z \rangle$ must decay faster so we assume the limits may be extended.

$$\begin{aligned} \frac{\langle M_z(t) M_z \rangle}{\langle M_z M_z \rangle} &= \exp \left[- \left(\frac{R'^2 I(I+1)}{S(S+1)} \int_{-\infty}^{\infty} e^{i\omega_0 \tau} \langle S_i^z(\tau) S_i^z \rangle d\tau \right) t \right] \\ &= \exp \left[- t / T_1 \right] \end{aligned} \quad (42)$$

$$\frac{1}{T_1} = \frac{R'^2 I(I+1)}{S(S+1)} 2\pi \langle S_i^z(\tau) S_i^z \rangle_{\omega_0} \quad (43)$$

Since the expression for $1/T_1$ involves the frequency dependent self-correlation function at ω_0 , it will probably not be too sensitive to the question of zero frequency divergence unless ω_0 is very small.

An expression for $1/T_2$ can be obtained from equation (19) under the same assumption that the limits on the t' integration can be extended to infinity.

$$\frac{1}{T_2} = \frac{I(I+1)}{S(S+1)} \pi \left[\mathcal{A}^2 \langle S_i^z(\tau) S_i^z \rangle_0 + \mathcal{A}'^2 \langle S_i^z(\tau) S_i^z \rangle_{\omega_0} \right] \quad (44)$$

Equation (44) is subject to suspicion if the zero frequency self-correlation function is too large. In that case, $1/T_2$, the resonance linewidth, must be determined numerically from equations (7), (13), and (19).

Combining equations (43) and (44) we obtain

$$\frac{T_1}{T_2} = \frac{1}{2} + \frac{\mathcal{A}^2 \langle S_i^z(\tau) S_i^z \rangle_0}{2 \mathcal{A}'^2 \langle S_i^z(\tau) S_i^z \rangle_{\omega_0}} \quad (45)$$

for the ratio of the relaxation times. For $H_0 \parallel a$ and $J' = .1J$ at 13.2 GHz we have

$$\left(\frac{T_1}{T_2} \right)_{H_0 \parallel a} \cong .6, \quad (46)$$

while for $H_0 \parallel c$

$$\left(\frac{T_1}{T_2} \right)_{H_0 \parallel c} \cong 13. \quad (47)$$

If J' is as small as .01J, we found previously that the linewidths ($\frac{2}{T_2}$) should be 53 Oe for $H_0 \parallel c$ and 6 Oe for $H_0 \parallel a$. If $1/T_1$ is calculated by equation (43) we find .39 Oe and 1.7 Oe, respectively for $H_0 \parallel c$ and $H_0 \parallel a$. These results give the following ratios for ω_0 equal to 13.2 GHz.

$$\left(\frac{T_1}{T_2}\right)_{H_0 \parallel a} \approx \frac{6}{2 \times 1.7} = 1.8 \quad (48)$$

$$\left(\frac{T_1}{T_2}\right)_{H_0 \parallel c} \approx \frac{53}{2 \times .39} = 68 \quad (49)$$

The results for T_1/T_2 obtained from the hyperfine interaction are considerably different for the two cases of $J' = .01J$ and $J' = .1J$. It is hoped that when the contributions to T_1 and T_2 from the dipolar interaction are added that there will still be a significant difference in the two cases. If this is so, experiments on the frequency dependence of T_1 and T_2 would indicate just how severe is the divergence near zero frequency of the two spin correlation functions.

IX. CONCLUSION

In conclusion, if a material exhibits linear chain properties then the usual theories of exchange narrowed lineshapes will have to be modified due to the steep rise near zero frequency of the two spin correlation functions. This may result in broader lines than would be expected. Many properties of CTS can be explained by assuming it has a linear chain structure, but the hyperfine ESR linewidth

and the Néel point, both of which depend on the interchain coupling, cannot be made simultaneously consistent with experimental data. The linear chain temperature dependence of $\langle S_1^z(\tau) S_1^z \rangle_\omega$, as calculated by the method of generalized diffusivity, cannot explain the large increase in linewidth as the temperature is lowered. Finally, frequency dependent measurements of T_1 and T_2 may indicate the severity of the divergence near zero frequency of $\langle S_1^z(\tau) S_1^z \rangle_\omega$.

REFERENCES

1. J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).
2. R. B. Griffiths, Phys. Rev. 135, A659 (1964).
3. F. Carboni and P. M. Richards, Phys. Rev. 177, 889 (1969).
4. H. Abe and K. Ôno, J. Phys. Soc., Japan 11, 947 (1956).
5. A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press, New York, 1961), pp. 98-101. D. Ter Haar, in Fluctuation Relaxation and Resonance in Magnetic Systems, edited by D. Ter Haar (Oliver and Boyd Ltd., Edinburgh, 1962), pp. 109-114. R. Kubo and K. Tomita, J. Phys. Soc., Japan, 9, 888 (1954).
6. P. M. Richards, Phys. Rev. 142, 189 (1966).
7. R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).
8. J. F. Fernandez and H. A. Gersh, Phys. Rev. 172, 341 (1968).
9. R. A. Tahir-Kheli and D. G. McFadden, Phys. Rev. 178, 800 (1969).
10. H. S. Bennett and P. C. Martin, Phys. Rev. 138, A608 (1965).
11. R. N. Rogers (private communication)
12. F. Mazzi, Acta Cryst. 8, 137 (1955).
13. R. N. Rogers, J. K. Pribram, and R. D. Lazay, Bull. Am. Phys. Soc. 9, 740 (1964). R. N. Rogers, F. Carboni, and P. M. Richards, Phys. Rev. Letters 19, 1016 (1967).
14. T. Oguchi, Phys. Rev. 133, A1098 (1964).
15. S. Saito, Physics Letters 24A, 442 (1967).
16. M. F. Collins, and W. Marshall, Proc. Phys. Soc. 92, 390 (1967).